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O$_2$($^1\Delta$) Yield Measurement by Raman Spectroscopy With Elimination of Chlorine Fluorescence Interference

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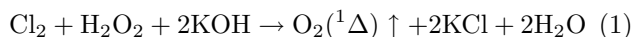
Deleterious chlorine fluorescence was found to occur at the same frequency as the Raman scattering of O$_2$($^1\Delta$) and O$_2$($^3\Sigma$), seriously affecting the O$_2$($^1\Delta$) yield measurement in the reaction of chlorine with basic hydrogen peroxide by use of the Raman spectroscopy technique. To solve this problem we have taken advantage of the fact that Raman radiation is always strongly polarized while fluorescence is essentially non-polarized in a gaseous medium. When chlorine utilization of a singlet oxygen generator is 88%, O$_2$($^1\Delta$) yield reaches (42.4±7.4)% with the effect of chlorine fluorescence completely eliminated.

Key words: Chemical oxygen iodine laser, Singlet oxygen yield, Spontaneous Raman spectroscopy, Chlorine fluorescence

I. INTRODUCTION

Molecular O$_2$($^1\Delta$) is the lowest singlet metastable oxygen, which plays an essential role in natural photochemical, photophysical, atmospheric and biological processes, besides serving as the energy source of the chemical oxygen iodine laser [1−3]. There are many different methods for producing O$_2$($^1\Delta$), in which the most effective one is the reaction of chlorine with basic hydrogen peroxide (BHP) [4−6]:

$$Cl_2 + H_2O_2 + 2KOH \rightarrow O_2(^1\Delta) \uparrow + 2KCl + 2H_2O \quad (1)$$

This reaction can give an O$_2$($^1\Delta$) yield Y_Δ as high as 70% [7−9], namely, the fraction of O$_2$($^1\Delta$) in total oxygen:

$$Y_\Delta = \frac{[O_2(^1\Delta)]}{[O_2(^1\Delta)] + [O_2(^3\Sigma)]} \quad (2)$$

where [O$_2$($^1\Delta$)] and [O$_2$($^3\Sigma$)] denote the concentration of singlet oxygen and ground state oxygen respectively. Thus, to get an accurate value of Y_Δ, one has to measure the concentration of both O$_2$($^1\Delta$) and O$_2$($^3\Sigma$) simultaneously and eliminate any interference to their measurements.

Gylys *et al.* developed a spontaneous Raman spectroscopy (SRS) technique for the direct measurement of O$_2$($^1\Delta$) yield [10, 11] by comparing the relative Raman intensities of O$_2$($^1\Delta$) and O$_2$($^3\Sigma$) scattering excited by a frequency-doubled YLF laser or a YAG laser

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[10−13]. However, the fluorescence of residual chlorine in reaction (1) [14] was found to occur in the same frequency range as the Raman scattering of O$_2$($^1\Delta$) and O$_2$($^3\Sigma$). Thus, when one measures O$_2$($^1\Delta$) yield with SRS, interference by chlorine fluorescence takes place. In 1978, Wolga proposed a universal method for separating radiation due to Raman scattering from the background of fluorescence by taking advantage of the fact that SRS radiation is strongly polarized while any fluorescence will be essentially non-polarized for gaseous species [15]. We applied this method for measuring Y_Δ of reaction (1) for the first time by setting up a system in which a polarizer is inserted between the Raman cell and the spectrograph. When chlorine utilization of SOG is 88%, we measure the O$_2$($^1\Delta$) yield Y_Δ to be (42.4±7.4)%. The error bar does not come from the interference of chlorine fluorescence, but from other noises.

II. THEORY

The gas sample is located at the origin of a Descartes coordinate system and irradiated by a plane polarized laser which propagates along Y axis and polarizes along X axis. The resulting Raman scattering and fluorescence is measured by the detector located at the Z axis. A polarizer is interposed between the sample and the detector. Assume polarization directions of the laser and the polarizer are $\vec{L}$ and $\vec{P}$ respectively, by rotating the polarizer for 90°, we can respectively get two signals representing the intensity of radiation in the parallel or perpendicular plane. Then the total light intensity is detected when $\vec{P}//\vec{L}$ and $\vec{P}\perp\vec{L}$ can be expressed as fol-

142

lows:

$$I_{t//} = I_{R//} + I_{F//} \tag{3}$$

$$I_{t\perp} = I_{R\perp} + I_{F\perp} \tag{4}$$

where $I_{R//}$ and $I_{F//}$ represent respectively Raman radiation and chlorine fluorescence intensities on the condition $\vec{P}//\vec{L}$, while $I_{R\perp}$ and $I_{F\perp}$ represent the Raman radiation and chlorine fluorescence intensities when $\vec{P}\perp\vec{L}$. The sum of the two can be expressed as:

$$
\begin{aligned}
I_s &= I_{t//} + I_{t\perp} \\
&= I_{R//} + I_{R\perp} + I_{F//} + I_{F\perp}
\end{aligned}
\tag{5}
$$

When there is no chlorine in the gas, the $O_2(^1\Delta)$ yield can be calculated by Eqs. (6) and (7) according to Eqs. (2) and (5):

$$
\begin{aligned}
Y_\Delta &= \frac{I_{s\Delta}/\sigma_{s\Delta}}{I_{s\Delta}/\sigma_{s\Delta} + I_{s\Sigma}/\sigma_{s\Sigma}} \\
&= \frac{I_{s\Delta}/[(1+\rho_\Delta)\sigma_{//\Delta}]}{I_{s\Delta}/[(1+\rho_\Delta)\sigma_{//\Delta}] + I_{s\Sigma}/[(1+\rho_\Sigma)\sigma_{//\Sigma}]} \\
&= \frac{I_{s\Delta}}{I_{s\Delta} + \theta_s I_{s\Sigma}}
\end{aligned}
\tag{6}
$$

$$
\begin{aligned}
\theta_s &= \frac{\sigma_{s\Delta}}{\sigma_{s\Sigma}} \\
&= \frac{\sigma_{//\Delta}}{\sigma_{//\Sigma}} \frac{1+\rho_\Delta}{1+\rho_\Sigma}
\end{aligned}
\tag{7}
$$

where $\rho_\Delta = I_{R\perp\Delta}/I_{R//\Delta}$ and $\rho_\Sigma = I_{R\perp\Sigma}/I_{R//\Sigma}$ are the depolarization ratios of $O_2(^1\Delta)$ and $O_2(^3\Sigma)$ respectively; $I_{R//\Delta}$ and $I_{R\perp\Delta}$ are the $O_2(^1\Delta)$ Raman intensities measured under the conditions of $\vec{P}//\vec{L}$ and $\vec{P}\perp\vec{L}$ respectively; $I_{R//\Sigma}$ and $I_{R\perp\Sigma}$ are the corresponding values for $O_2(^3\Sigma)$ under $\vec{P}//\vec{L}$ and $\vec{P}\perp\vec{L}$ respectively. $I_{s\Delta}=I_{R//\Delta}+I_{R\perp\Delta}$ and $I_{s\Sigma}=I_{R//\Sigma}+I_{R\perp\Sigma}$ are the total Raman radiation intensities of $O_2(^1\Delta)$ and $O_2(^3\Sigma)$ respectively. $\sigma_{//\Delta}$ and $\sigma_{//\Sigma}$ are the Raman cross sections of $O_2(^1\Delta)$ and $O_2(^3\Sigma)$ measured in $\vec{P}//\vec{L}$ respectively; $\sigma_{s\Delta}=\sigma_{//\Delta}(1+\rho_\Delta)$ and $\sigma_{s\Sigma}=\sigma_{//\Sigma}(1+\rho_\Sigma)$ are the Raman cross sections corresponding to $I_{s\Delta}$ and $I_{s\Sigma}$; θ_s is the ratio of Raman cross section $\sigma_{s\Delta}$ and $\sigma_{s\Sigma}$.

Gylys et al. used Eqs. (6) and (7) to calculate the $O_2(^1\Delta)$ yield [10, 11]. However, when there is chlorine in the gas, Eqs. (6) and (7) cannot be used because I_s includes the fluorescence terms. As fluorescence is essentially non-polarized for gases, namely, $I_{F//}=I_{F\perp}$, the Raman radiation intensity after eliminating the fluorescence can be obtained as follows [15]:

$$
\begin{aligned}
I_d &= I_{t//} - I_{t\perp} \\
&= I_{R//} - I_{R\perp}
\end{aligned}
\tag{8}
$$

Thus, the $O_2(^1\Delta)$ yield can be calculated by Eqs. (9) and (10) according to Eqs. (2) and (8):

$$Y_\Delta = \frac{I_{d\Delta}/\sigma_{d\Delta}}{I_{d\Delta}/\sigma_{d\Delta} + I_{d\Sigma}/\sigma_{d\Sigma}}$$
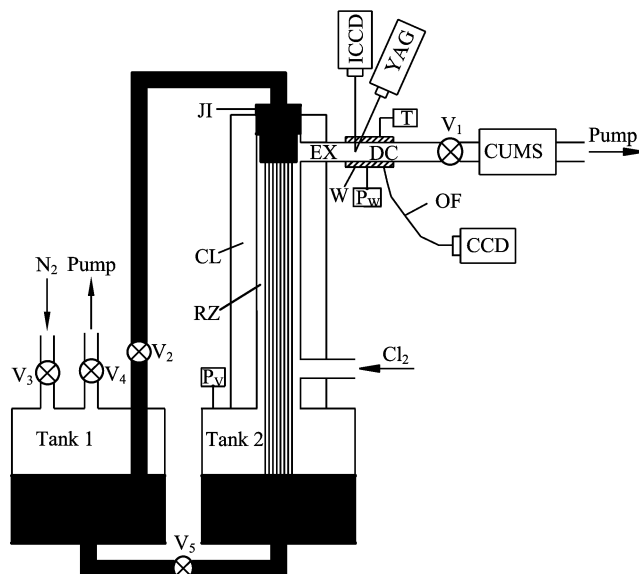

FIG. 1 Schematic of experimental setup. JI: Jet injector; CL: Reaction cylinder; RZ: Reaction zone; W: Quartz window; DC: Diagnostic cell; YAG: 532 nm frequency-doubled YAG laser; ICCD: ICCD spectrograph; OF: Optical Fiber; CCD: CCD spectrograph; CUMS: Cl_2 utilization measuring system; P_V, P_W: Manometer; T: Thermocouple; Tank 1: pressurized BHP tank; Tank 2: BHP collection tank; V_1-V_5: Valve; EX: Exit for $O_2(^1\Delta)$ gas flow.

$$
\begin{aligned}
&= \frac{I_{d\Delta}/[(1-\rho_\Delta)\sigma_{//\Delta}]}{I_{d\Delta}/[(1-\rho_\Delta)\sigma_{//\Delta}] + I_{d\Sigma}/[(1-\rho_\Sigma)\sigma_{//\Sigma}]} \\
&= \frac{I_{d\Delta}}{I_{d\Delta} + \theta_d I_{d\Sigma}}
\end{aligned}
\tag{9}
$$

$$
\begin{aligned}
\theta_d &= \frac{\sigma_{d\Delta}}{\sigma_{d\Sigma}} = \frac{\sigma_{//\Delta}}{\sigma_{//\Sigma}} \frac{1-\rho_\Delta}{1-\rho_\Sigma} \\
&= \theta_s \frac{1-\rho_\Delta}{1+\rho_\Delta} \frac{1+\rho_\Sigma}{1-\rho_\Sigma}
\end{aligned}
\tag{10}
$$

where $I_{d\Delta}=I_{R//\Delta}-I_{R\perp\Delta}$ is the difference of the Raman intensities of $O_2(^1\Delta)$ in $\vec{P}//\vec{L}$ and $\vec{P}\perp\vec{L}$. $I_{d\Sigma}=I_{R//\Sigma}-I_{R\perp\Sigma}$ is the corresponding difference value for $O_2(^3\Sigma)$. $\sigma_{d\Delta}=\sigma_{//\Delta}(1-\rho_\Delta)$ and $\sigma_{d\Sigma}=\sigma_{//\Sigma}(1-\rho_\Sigma)$ are the Raman cross sections corresponding to $I_{d\Delta}$ and $I_{d\Sigma}$. θ_d is the ratio of Raman cross section $\sigma_{d\Delta}$ and $\sigma_{d\Sigma}$.

As long as θ_s, ρ_Δ and ρ_Σ are known, the $O_2(^1\Delta)$ yield can be calculated according to Eqs. (9) and (10). In fact, θ_s has been determined by Gylys et al. to be 0.45 ± 0.03 [16]. The values of the depolarization ratio of $O_2(^1\Delta)$ and $O_2(^3\Sigma)$, ρ_Δ and ρ_Σ, have been measured in this work. The former is so far not reported in literature, while the latter agrees well with the value of other reports [17−19].
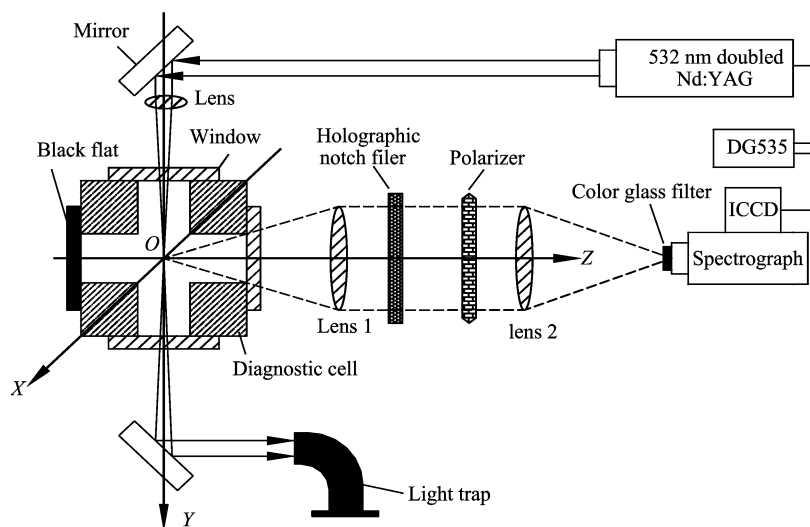

FIG. 2 Schematic of the spontaneous Raman spectroscopy system with elimination of interference from chlorine fluorescence.

III. EXPERIMENTS

The schematic of the experimental setup is shown in Fig.1, which has been described in Ref.[8]. BHP is prepared with 7 L of 50%H_2O_2 and 10 kg of 50%KOH aqueous solution and kept in tank 1 at about -14 °C. Under the N_2 pressure, the BHP flows through 0.8 mm diameter nozzles with the amount of 19 (JI) to form the jet streams that eject BHP to the reaction cylinder of 16 cm length and 1 cm inner diameter. Both the injector and cylinder are made of plexiglas. The gaseous Cl_2 enters from the bottom, flowing up in counter-flow to the BHP streams. The gaseous product including $O_2(^1\Delta)$, $O_2(^3\Sigma)$, the residual Cl_2, a small amount of $O_2(^1\Sigma)$ and water vapor, flows out through the top exit (EX) and enters the diagnostic cell (DC), where the $O_2(^1\Delta)$ yield (Y_Δ) is measured by the Raman spectra of $O_2(^1\Delta)$ and $O_2(^3\Sigma)$ excited by the 532 nm light of a frequency-double YAG laser. A CCD spectrograph is also mounted on the front of the DC's window to record the spectra of $2O_2(^1\Delta)\rightarrow 2O_2(^3\Sigma)$ cooperative emission together with the $O_2(^1\Sigma)\rightarrow O_2(^3\Sigma)$ spontaneous emission. Then, the water vapor content in the gas phase can be calculated from the light intensity ratio of the peak at 634 nm versus that at 762 nm [20]. A chlorine utilization measuring instrument (CUMS) is located downstream the diagnostic cell. By measuring the UV (334 nm) absorption rate of Cl_2 before and after the reaction with BHP, the chlorine utilization can be calculated using the Beer-Lambert law [21].

The setup for $O_2(^1\Delta)$ yield measurement is shown in Fig.2. The frequency-doubled YAG laser operates at a pulse repetition rate of 5 kHz with a pulse length of 300 ns and an average power of 12 W. The origin of a Descartes coordinate system is located at the center of the diagnostic cell, X and Y axis is the direction of laser polarization and propagation respectively, and XY plane is the polarization plane of the laser. The resulting Raman scattering and Cl_2 fluorescence are collected in the Z axis direction, focused onto the slits of an $f/4.0$ Acton imaging spectrograph through two lenses, a holographic notch filter and a color glass filter, and then recorded using a Princeton instruments 1024×256 ICCD. A DG-535 digital delay/pulse generator synchronously controls the time delay of the laser pulse and ICCD gate, making sure that the ICCD gate opens only in the laser pulse duration.

In order to eliminate the Cl_2 fluorescence, a polarizer whose polarization plane can rotate along Z axis is interposed between lens 1 and 2. When the polarization plane of the polarizer is parallel to the laser polarization direction, the signal collected by ICCD is $I_{t//}$. On the other hand, when the polarization plane of polarizer is perpendicular to laser polarization direction, the signal collected by ICCD is $I_{t\perp}$. According to the context mentioned above, the difference of $I_{t//}$ and $I_{t\perp}$ is then the Raman radiation intensity with Cl_2 fluorescence eliminated. Calibration was made to the signals collected by ICCD to account for the different grating efficiency for light polarized perpendicular to the grating rulings and parallel to them.

IV. RESULTS AND DISCUSSION

Figure 3 shows a typical spectrum recorded when chlorine utilization of the singlet oxygen generator (SOG) is 100% complete. It can be seen that the curve is clean and Raman radiation intensities of $O_2(^1\Delta)$ and $O_2(^3\Sigma)$ can be easily measured and thus the corresponding $O_2(^1\Delta)$ yield can be calculated when there is no residual chlorine. However, as shown in Fig.4, when chlorine utilization of SOG is 90%, fluorescence of chlorine appears which overlaps with the Raman scattering
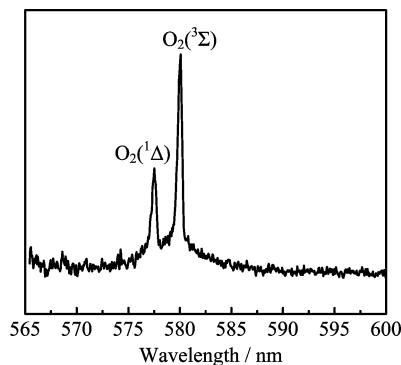
FIG. 3 Raman spectrum of $O_2(^1\Delta)$ and $O_2(^3\Sigma)$ collected by the conventional spontaneous Raman spectroscopy system when chlorine utilization is 100%.
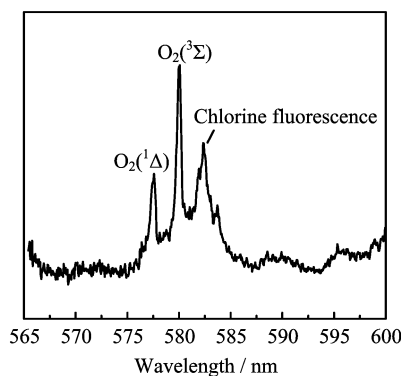

FIG. 4 Raman spectrum of $O_2(^1\Delta)$ and $O_2(^3\Sigma)$ and chlorine fluorescence collected by the conventional spontaneous Raman spectroscopy system when chlorine utilization is 90%.

spectroscopy of $O_2(^1\Delta)$ and $O_2(^3\Sigma)$. Thus the measurement of $O_2(^1\Delta)$ yield will be affected. If the chlorine utilization is even low, the Raman signal can be completely buried in the deleterious chlorine fluorescence, the measurement will failed.

Figure 5 shows the spectrum collected by the system shown in Fig.2 when chlorine utilization of SOG is 88%. It can be seen from Fig.5 that the intensities of chlorine spectra are essentially the same when the polarization plane of the polarizer is either parallel or perpendicular to the polarization plane of the laser while the Raman intensities of $O_2(^1\Delta)$ and $O_2(^3\Sigma)$ are entirely different in the two conditions. So it is clear that we can use Eqs. (9) and (10) to calculate the yield of $O_2(^1\Delta)$ with complete elimination of the interference of chlorine.

To determine the Raman cross section ratio of $O_2(^1\Delta)$ and $O_2(^3\Sigma)$ (θ_d), first one has to know the depolarization ratios of $O_2(^1\Delta)$ and $O_2(^3\Sigma)$. These two values can be determined by measuring the intensities of $O_2(^1\Delta)$ and $O_2(^3\Sigma)$ Raman radiations that are parallel or perpendicular to the polarization direction of laser in the condition that chlorine utilization of SOG is 100% as shown in Fig.6. For $O_2(^3\Sigma)$, it is determined to be
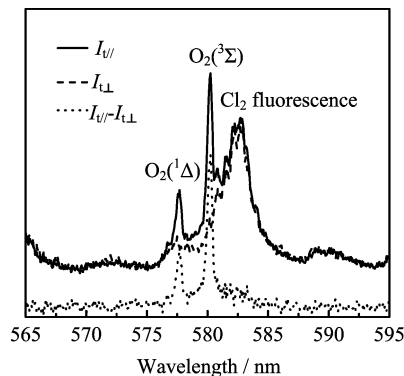
FIG. 5 Spectra collected by the system of Fig.2, when chlorine utilization of SOG is 88%. $I_{t//}$: Spectrum collected when polarization plane of polarizer is parallel to the polarization plane of laser. $I_{t\perp}$: Spectrum collected when polarization plane of polarizer is perpendicular to the polarization plane of laser. $I_{t//}$-$I_{t\perp}$: Difference of $I_{t//}$ and $I_{t\perp}$.
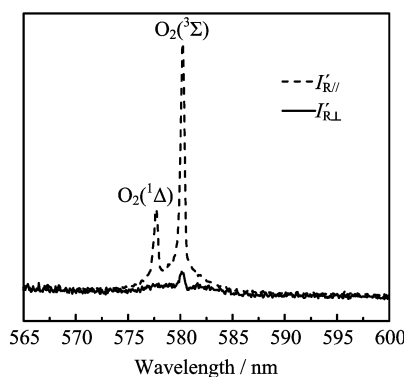

FIG. 6 Spectra collected in the conditions that polarization direction of polarizer is parallel to and perpendicular to the polarization direction of laser. $I'_{R//}$: The spectrum collected under the condition that polarization direction of polarizer is parallel to the polarization direction of laser. $I'_{R\perp}$: The spectrum collected under the condition that polarization direction of polarizer is perpendicular to the polarization direction of laser. In both cases, the chlorine utilization of SOG is 100%.

$I'_{R//\Sigma}$=71.67±0.95 and $I'_{R\perp\Sigma}$=4.85±0.75, and the depolarization ratio to be ρ_Σ=0.067±0.011, which agrees well with that reported in literatures [17−19]. For $O_2(^1\Delta)$, $I'_{R//\Delta}$=21.13±0.83, but $I'_{R\perp\Delta}$ cannot be determined because the corresponding spectrum is buried in noise. The maximum value of $I'_{R\perp\Delta}$ should be smaller than the area of the noise in the region of $O_2(^1\Delta)$ Raman spectroscopy, which is determined to be 1.065. Then, ρ_Δ has a value in the region of 0 to 0.050. Introduce these values of ρ_Δ and ρ_Σ into Eq.(10), we get the Raman cross section ratio θ_d=0.49±0.07. The relative error of θ_d is calculated by the following expression:

$$\frac{\mathrm{d}\theta_d}{\theta_d} = \left|\frac{\mathrm{d}\theta_s}{\theta_s}\right| + \frac{2\rho_\Delta}{1-\rho_\Delta^2}\left|\frac{\mathrm{d}\rho_\Delta}{\rho_\Delta}\right| + \frac{2\rho_\Sigma}{1-\rho_\Sigma^2}\left|\frac{\mathrm{d}\rho_\Sigma}{\rho_\Sigma}\right| \quad (11)$$

TABLE I Relative errors of various error sources and their contributions to the relative error of $O_2(^1\Delta)$ yield measured in Fig.5 (total contribution is 17.5%).

Error source	θ_s	$I'_{R\perp\Delta}$	$I'_{R//\Delta}$	$I'_{R\perp\Sigma}$	$I'_{R//\Sigma}$	$I_{d\Delta}$	$I_{d\Sigma}$
Relative error/%	6.67 [16]	100	3.9	15.5	1.3	12.1	4.1
Contribution/%	3.8	2.9	0.1	1.2	0.1	7.0	2.4

The relative error of $O_2(^1\Delta)$ yield with chlorine fluorescence that can be calculated by the following expression:

$$\left|\frac{dY}{Y}\right| = \frac{\theta_d I_{d\Sigma}}{I_{d\Delta} + \theta_d I_{d\Sigma}}\left[\left|\frac{d\theta_d}{\theta_d}\right| + \left|\frac{dI_{d\Delta}}{I_{d\Delta}}\right| + \left|\frac{dI_{d\Sigma}}{I_{d\Sigma}}\right|\right] \quad (12)$$

Table I lists the relative errors of various error sources and their contributions to the relative error of $O_2(^1\Delta)$ yield measured in Fig.5. The corresponding $O_2(^1\Delta)$ yield can be determined to be $(42.4\pm7.4)\%$ according to Eqs. (9)−(12).

By comparing the contributions of these seven terms to the relative error of $O_2(^1\Delta)$ yield, two conclusions can be drawn: (i) although the relative error of $I'_{R\perp\Delta}$ is large, its contribution to the relative error of $O_2(^1\Delta)$ yield is small; and (ii) the relative error of $O_2(^1\Delta)$ yield mainly comes from the low Raman signal-to-noise ratio. We may solve this problem by adopting several measures, such as increasing the average power of YAG laser from 12 W to ∼150 W, increasing the numerical aperture of monochromator from $f/4.0$ to $f/1.8$, *etc.*

V. CONCLUSION

We have applied Wolga's idea [15] to build a system for measuring the yield of $O_2(^1\Delta)$ by Raman scattering in the reaction of chlorine with basic hydrogen peroxide. When chlorine utilization of SOG is 88%, we get $Y_\Delta=(42.4\pm7.4)\%$ with the completely eliminated effect of chlorine fluorescence. The rather large relative error of $O_2(^1\Delta)$ yield mainly comes from the low Raman signal-to-noise ratio. We may improve this issue by adopting several measures, such as increasing the average power of laser and the numerical aperture of monochromator, *etc.*

VI. ACKNOWLEDGMENTS

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